Method for Manufacturing Parts, Use Thereof, Workpiece Stored in Air, and Vacuum Processing Chamber

The present invention relates to a method for manufacturing parts according to the preamble of Claim 1, uses of this method according to Claims 15 to 18, a workpiece stored in air according to Claim 19, as well as a vacuum processing chamber according to Claim 20.

Definitions:

The term "intimate connecting method" is understood to include bonding (welding, soldering), gluing, potting, and coating, especially in a vacuum coating process, whether PVD or CVD or methods derived therefrom, as well as so-called "direct bonding," in which carefully cleaned surfaces are connected to one another directly by interatomic forces, as used for example in direct wafer bonding of silicon on silicon, silicon on SiO_2, and also in the joining of metal surfaces with one another or of metal surfaces with silicon surfaces, for example CuSi or Au-Si. In these connections, at least one of the surfaces to be joined intimately is always the surface of a solid body.

The following in particular are addressed within the framework of the present invention:

— metal surfaces, especially made of Cu, Ni, Ag, Au Pd, Sn, Ti, In, or alloys containing at least one of these metals;

— semi-metallic surfaces, especially made of silicon, germanium, boron, carbon, gallium arsenide, gallium nitride, silicon carbide, zinc oxide, or of a material with at least one of these semi-metals;

— ceramic surfaces, especially made of quartz, aluminum oxide, aluminum nitride, zirconium oxide, boron nitride, diamond, and silicon nitride;

-- plastic surfaces on an epoxy or ester basis, polyimides, polyvinyl chlorides, polyethylene, polystyrene, polyolymethacrylate, polyamide, polyurethane, phenoplasts, phenol resins, siloxanes, Teflon;

-- in particular, metals like those that are typically used in packaging processes for semiconductors, namely cured epoxy resins, HLST materials (semiconductor system substrates) made of epoxy (epoxy base laminate substrates), solder resist, photo-resist, etc..

It is important that those surfaces which undergo intimate connection can consist of portions different from the various materials named. The energy supply for the intimate connection in most cases is of a thermal nature and is supplied for example by heated tools, Joule heat, UV radiation, or preferably by ultrasound to the surfaces to be joined, or by reaction energy during gluing and possibly also during potting.

The present invention in is used especially advantageously in packaging integrated circuits. In this sense, its primary area of application lies in the field of the semiconductor industry. However, the present invention can also be used for other areas of technology, basically in all those in which, within the framework of the manufacturing method according to the invention, before the creation of an intimate connection, organic or organic/oxidic contaminating compounds must be removed from the (at least one) surface of the solid body.

Although surface materials have been defined above for which the present invention is known to be suitable, it should be noted that other surface materials, for example oxides, nitrides, carbides, oxynitrides, oxycarbides, carbonitrides, and oxycarbonitrides of at least one of the metals Ti, Ta, Zr, and Hr can be processed according to the invention, especially if the intimate connection by the coating is taken into account.

As mentioned above, the procedure according to the invention is also especially suitable for the surfaces of solid bodies that consist of different materials, especially areas that contain different materials. As far as intimate connection is concerned, such multi-material surfaces pose especially difficult problems.

In the so-called packaging of integrated circuits, as a preferred area of application of the present invention, a distinction is made between a plurality of work steps that include an intimate connection of surfaces in the above sense:

1. The individual integrated circuits are cut from a silicon wafer, mounted on semiconductor system carriers (HLST) and joined with them (so-called "die-bonding"). The HLST surface to be joined is usually made of copper or nickel, silver, or gold, and/or from a material with an epoxy basis, generally from a plastic as mentioned above . Examples of such HLSTs are stamped or etched metal lead frames, ceramic substrates, or BGA (ball grid arrays) — substrate carriers made of plastic or printed circuit boards. The connecting methods used include hard soldering, soft soldering, and gluing. In flip chip soldering processes, the integrated circuit is mounted on an HLST by means of geometrically separate solder balls which are simultaneously used as I/O contacts.

2. Joining the integrated circuits with contact supporting points on the HLST, for example on the "lead frames:" The surfaces involved are metallic, made for example of Al, Au, Cu, Ni, Pd, Ag, Pb, Sn or alloys of these metals. In this case, soldering or welding are primarily used as joining techniques, especially fluxless soldering or ultrasonic welding. This step is known as "wire bonding".

3. Molding: In this method step, the circuits on the HLST, for example the lead frames, following "wire bonding" are potted with a molding compound, with the abovementioned surfaces of the HLST and the integrated circuits being involved with the molding compound.

A cleaning method is known from EP-0 371 693 within the framework of a manufacturing method in which the surfaces later to be connected in the manner described above exclusively by applying energy are first exposed to a microwave plasma discharge in a vacuum atmosphere containing hydrogen. Then, without breaking the vacuum, the solder layer provided for connecting the surfaces is melted by the plasma discharge. Thus, a contaminated surface coating that would seriously interfere with subsequent joining processes is prevented simply by avoiding contact with air.

It is also known from US Patent 5,409,543 to use activated hydrogen to prepare for a soldering process. As a result, an oxide layer is singled out for the performance of the soldering process on the metal surface.

It is also known from EP-A-0 427 020 to pickle a passive and oxide layer of assembly partners by means of a high-frequency plasma pre-treatment with a processing gas, in other words to separate it out. The processing gases that can be used include the following gases and mixtures of the gases

among others: O_2, H_2, Cl_2, N_2O, N_2, CF_4, etc.. The abovementioned pickling does not take place immediately before the soldering process as in US Patent 5,409,543,so that the partners to be joined are stored in protective intermediate storage locations, for which purpose suitable containers under a protective gas are provided to prevent contamination.

Within the framework of the three packaging steps mentioned above, two plasma processing steps have been introduced in the meanwhile. They are intended primarily for substrate carrier materials made of plastic ("plastic ball grid arrays — PBGA"). The plasma processing before the "wire bonding" (Step 2) serves to clean the surfaces of the metal contact support points ("contact pads") usually made of aluminum, on the die (the chip) and the contact support points that are usually made of gold on the system substrate (HLST), so that electrical contact with the connecting wire, usually gold wire, is ensured. The most important source of contamination of these contact support pads is a previous treatment process ("curing") that is used for curing an epoxy adhesive used in the abovementioned Step 1.

A second plasma treatment usually takes place only after the "wire bonding" (Step 2), prior to the "molding" process step (Step 3). This is intended to achieve an improved adhesion of the molding material.

Both of the plasma processing steps mentioned above were usually performed in a vacuum under plasma gas excitation. A high-frequency, microwave, or ECR plasma is usually employed. The plasma surface interaction and the cleaning process associated with it or the surface modification takes place by sputtering and/or a chemical reaction with plasma-excited gases. For sputtering in a non-active atmosphere, usually it

only argon is used and the self-bias potential of the substrate to be cleaned and operated floating is utilized to accelerate argon ions toward the latter and to achieve the desired removal of the cleaning material. In plasma-chemical removal, reactive gases, for example oxygen, are excited, dissociated, or ionized and then enter into a reaction with surface impurities, for example carbon, and carry away the gaseous reaction products such as CO_2 through the pumping system.

As in the present case, a highly advantageous processing method has become known from WO 97/39472, by using it as the abovementioned plasma processing method. In this process, hydrogen is excited preferably in a plasma discharge and then removes carbon from surfaces (for example as CH_4) while simultaneously reducing oxides on the surfaces involved, to produce H_2O gas. Sputtering is avoided, which involves the risk of redeposition, and the abovementioned process can be applied without limit to metallic substrate carrier materials or silver contact surfaces as well, that would oxidize severely in an atmosphere containing the excited oxygen, especially in a plasma containing oxygen. This would lead to an adverse effect on "wire bondability" or "moldability" (see above, Steps 2 and 3). This is also particularly important if applications for the modern copper metallization of chips is being considered. One very important property of this process is that the surfaces are passivated for a technologically sufficient period of time by the hydrogen plasma and so can be stored in air before entering into an intimate connection in the above sense.

The disadvantage of the known process is that the process window, in other words the range of process parameters still depends to a certain degree on the material of the surfaces to be processed and to be joined intimately later. Thus for example the plasma processing of substrate carrier

materials (strips) normally takes place in magazines. These magazines have slits so that the gases excited in the plasma can penetrate to reach the substrate surfaces to be treated in the magazine and the volatile reaction products of easily can leave the magazine cleaning and be pumped off. The substrate surfaces, especially in the case of PBGA ("plastic ball grid array") strips, always consist of a plurality of different materials. The "solder resist" is a long-chain organic compound, the surface of the "die " (chip) consists for example of polyimide or silicon nitride, the metallization part usually consists of aluminum and gold. It can never be ruled out that additional organic impurities remain on the surface of the "solder resist" that originate on strips from previous processes, e.g. cleaning steps, are precipitated during the curing of the epoxy in the "curing process", or result from the deliberate surface treatments on the "solder resist," treatments to promote for example the wettability with the molding material. Highly volatile compounds may also be present that evaporate in particular at the beginning of the abovementioned plasma treatment, especially in the abovementioned magazines, generally in small spaces, resulting in locally high pressures, and it can happen that the chemical equilibrium is altered by these by the local pressure shifts so that no more hydrocarbons can be removed from the reactive hydrogen in the abovementioned process, but it promotes polymerization. The result of such re-covering can be extremely diverse. Thus for example, at the contact support points ("contact pads") the "wire bondability" relative to the pull strength achieved is reduced, or much longer processing times are required in order to remove the deposited layer again at optimum pressure and possibly at higher temperature. Because of the abovementioned diversity of materials on the surface to be treated, however, a prolonged processing time or a more intense plasma processing can for example treat some surfaces such as metal surfaces, better while at the same time, others, such as the "solder resist" or the passivation layer

can be changed so that the adhesion of the molding material to be added later is made worse (see the discussion of Tests II).

The goal of the present invention is to provide a method for manufacturing parts of the species recited at the outset in which the process window, especially the pre-treatment processing window, especially its dependence on various surface materials, but also on process parameters, especially on the parameters "pressure" and "temperature," is widened. In other words, the method proposed according to the invention, under expanded parameter ranges, such as pressure ranges and/or temperature ranges, is intended to provide uniformly satisfactory results over the entire variety of materials mentioned, as far as the quality of intimate connection to be provided later is concerned.

On the basis of this enlarged process window, an improved homogenization of the processing effect distribution is also to be ensured on multi-material surfaces.

As mentioned above, in particular, the results should also be ensured for substrates in magazines or for substrates with narrow geometries (slits and holes). Since the plasma-chemical reactions on the substrate surfaces also depend on the substrate temperature and larger temperature gradients are involved, especially for plasma processing in magazines and on extensive substrates, the abovementioned process window enlargement is also intended to promote uniformity.

Thus, a constant surface treatment, including gap surfaces, hole surfaces, groove surfaces, etc. is to be made possible on substrates themselves.

In addition, the re-covering of the treated surface by deposition or polymerization is to be prevented, the method should be economical, and no explosives and/or environmentally hazardous gases should be used. On the other hand, the advantages of the known methods mentioned last according to WO 97/39472, especially its preservative properties, are to be maintained.

The following definitions apply:

-- passivation or passivized; see Römpps Chemielexikon, Franksche Vrelagshandlung, Stuttgart, 9th Edition, Page 3005.

This term refers to a bonded protective coating on the surface of the solid. The clean solid body surface is protected against atmospheric air influences . This is accomplished for example by forming an oxide or nitride layer. Such a layer must first be broken up by energy applied specifically for this purpose for producing an intimate connection of the type described above, for example by application of higher temperatures than required for the actual joining process, or chemically, for example by using a flux.

-- we make a basic distinction between the abovementioned passivation and preservation which in particular does not require any layer separation by additional energy for joining . This preservation is known in conjunction with the invention in accordance with WO 97/39472, with reference being made in full to this document and this document is declared to be an integral element of the present specification.

The solution to the above problem is provided by the method of the type recited at the outset and implemented in accordance with the characterizing

clause of Claim 1. Accordingly, the pre-treatment is performed using plasma-activated gas that contains nitrogen.

In addition, in a preferred embodiment of a manufacturing method according to the invention, the plasma-activated gas also contains hydrogen.

Although it is quite possible to use any one of the many known plasma discharge types for plasma activation of the abovementioned gases, in a preferred embodiment the abovementioned plasma discharge is produced as a low-voltage discharge, preferably with a thermionic cathode.

In addition, the plasma-activated gas preferably contains a working gas, preferably a noble gas, especially argon.

Even if the abovementioned plasma-activated gas, in addition to nitrogen, contain certain gas components, especially hydrogen and/or a working gas, it contains in a preferred manner primarily nitrogen, and even consists of nitrogen apart from any working gas that might be provided.

The solid body surfaces to be joined intimately are materials that are metallic and/or semi-metallic and/or ceramic and/or consist of plastic, especially according to the materials mentioned at the outset and deemed preferred. Especially preferentially, the abovementioned solid book solid body surfaces are surfaces with areas composed of different materials, especially the materials mentioned.

The intimate connection is formed by the manufacturing method according to the invention, preferably by gluing, soldering, welding, molding, or coating, especially vacuum coating, performed by so-called "direct

bonding."

The abovementioned preferentially used low-voltage discharge is also operated preferentially with a discharge voltage of 30 V or more, preferably with a discharge current between 10 A and 300 A, including both limits, especially at 40 A to 70 A.

In an especially preferred embodiment of the method according to the invention, the (at least one) solid body surface to be connected intimately later, following the abovementioned pretreatment and prior to its intimate connection, is exposed to air, for periods ranging from days to weeks.

This makes it possible not to process further the abovementioned surface immediately after its pretreatment and not necessarily at the same location; the result is a high degree of flexibility regarding rhythm and processing location for working the method according to the invention without additional costly cleanliness precautions such as storage under a protective gas, being provided.

In an especially preferred embodiment of the method according to the invention, (at least the one) solid body phase is stored in a holder during pre-treatment, said holder defining access areas on the abovementioned surface that are narrowed relative to the plasma discharge chamber. In the overwhelming majority of cases, the (at least one) solid body phase is formed by a disk- or plate-shaped substrate, and the holding device is provided with at least one access slit.

Preferably, the holding system has several of the abovementioned access slits and forms an actual magazine.

One preferred use of the method according to the invention consists in joining integrated circuits with HLST or in the electrical connection of integrated circuits by "wire bonding," or for sheathing electrical circuits connected with HLST and connected by "wire bonding" with a molding material.

Another preferred use is for integrated circuits for flip chip connection and for positioning. Firstly, the soldering points can be cleaned of oxide and passivated at the same time and secondly, following plasma processing, a better wetting of the so-called "underfill" (a molding material that fills the gap between the chip and the chip carrier and which serves to absorb mechanical stresses) is achieved.

In addition , the method according to the invention is also used preferably for workpieces of the type specified in Claim 17. The method according to the invention is also especially suitable for chips with copper traces, according to Claim 18.

The workpiece that has been processed with plasma according to the invention and stored in air is characterized by the fact that the abovementioned surface that has been exposed to air has an increased nitrogen concentration by comparison with a directly produced surface of the workpiece which however was not stored in air, something that can be demonstrated for example by "Fourier transform infrared spectroscopy" with "attenuated total reflection," FTIS-ATR,, and/or with "nuclear reaction analysis," NRA, or with "time-of-flight secondary ion mass spectrometry," or TOP-SIMS. As a result of the elevated nitrogen concentration, which indicates the pre-treatment according to the invention, it is possible to use the workpiece according to the invention and stored in air directly and

without additional pretreatment in the above sense for an intimate connection. It will be possible in another preferred embodiment of the method according to the invention to perform the intimate connection by the influence of heat on air, preferably at a solid body temperature of 150°C at most.

A vacuum processing chamber according to the invention is also characterized according to the wording of Claim 20 and with preferred embodiments according to Claims 21 and 22.

In summary it may be said that the influence of nitrogen as recognized and utilized according to the invention is surprising, in the light of the teaching in the art (see J.L. Vossen et al., "Thin Film Processes," Academic Press, Inc. 1978) according to which nitrogen plasmas did not remove polymer surfaces.

The invention will now be described in greater detail with reference to the figures and examples.

Figure 1 shows schematically the structure of a system according to the invention as used for the experiments described.

Figure 2 shows the Auger spectrum of copper surfaces ("lead frames") for producing a soft-soldered connection;

Figure 3 shows schematically the definition of tensile stress or pull strength F_P of "wire bond" connections;

Figure 4 shows the results of tensile stress capacity tests ("pull strength"),

performed as indicated with reference to Figure 3, with hydrogen-argon plasma processing (a), argon plasma processing (b), treatment in an $Ar/N_2/H_2$ plasma (c), and processing in an argon/nitrogen plasma (d),

Figure 5, on the basis of a time/pull strength graph, shows the long-term effect of the plasma processing used according to the invention and the pull strength of intimate connections formed on workpieces according to the invention;

Figure 6, by analogy with the drawing in Figure 4, shows the results of additional pull strength tests; and

Figure 7 shows schematically in cross section, areas of substrates that are also suitable for using the method according to the invention.

As mentioned above, in the manufacturing method according to the invention, the plasma discharge for exciting the gas is preferably designed as a low-voltage arc discharge. Systems of the type used preferentially are known, for example from:

-- DE-OS 43 10 941, corresponding to U.S. Patent 5,384,018;

-- DE-4 029 270, corresponding to EP-478 909 and DE-4 029 268, corresponding to U.S. Patent 5,336,326;

-- EP-510 340 corresponding to U.S. Patent 5,308,950.

These documents, provided only as examples, show all of the processing chambers for workpieces using low voltage arc discharges. As far as the

design of such processing chambers is concerned, these documents should form an integral part of the present specification.

In Figure 1, a preferred system for use according to the present invention is shown. In a cathode chamber 1, a thermionic cathode 3 is mounted, insulated. Parts 17 of cathode chamber 1 surround a diaphragm opening 9. Cathode chamber 1 is mounted by insulating supports 22 on the wall of processing chamber 11. It includes a shield 20, which is operated with floating potential, relative to both the cathode chamber 1 and also relative to processing chamber 11, the parts 17 at the dark space distance d up to directly into the area of diaphragm opening 9. The thermionic cathode is operated by means of a source 24 with heating current I_H and is guided by a voltage source 26 and, generally speaking, a unit 28 on at least a part of the cathode chamber wall, preferably on the cathode chamber wall itself. Unit 28 acts as a current limiter and causes a voltage drop u in the function of the current i flowing through it. As indicated by the dashed lines, it can be in the form of a current-controlled voltage source but is preferably in the form of a passive circuit element, especially a resistance element 30.

The positive pole of voltage source 26 can be set to a reference potential, either ground or another specified potential, or can be operated in a potential-free manner as shown purely schematically by the possibility switch 32. Similarly, since it is electrically insulated from cathode chamber 1, the processing chamber 11, as shown purely schematically with possibility switch 34, can be operated at ground potential, a reference potential, or possibly even at a floating potential. The processing chamber inside wall 36 or at least parts thereof can be connected as the anode relative to the thermionic cathode 3; preferably however a separate anode 38 as indicated by the dashed lines, can be provided which is connected by

a voltage source 40 relative to the thermionic cathode 3 as an anode, i.e. positively. Anode 38 is then used preferably as the workpiece carrier for the workpieces W shown schematically. A working gas is supplied through gas supply line 41 to the cathode chamber, said gas preferably being argon for example. Through another gas supply line 40 shown schematically, as indicated schematically by the possibility switch 35, depending on the potential connection, chamber 11 can be connected to the potential, the gas G (X, Y, N_2) containing the nitrogen, preferably nitrogen, is supplied by a gas tank arrangement 50. The gas G is admitted by a valve 52 shown schematically .

Especially in the industrial application of the method according to the invention, a magazine 51 is used as the workpiece carrier 51, with the processing chamber according to the invention shown schematically in Figure 1. A plurality of substrates to be processed is stacked therein and connected only by insertion slits on the front and/or rear for the substrates, as well as access slits 51a additionally provided in the magazine wall. The geometric ratio H relative to the remaining communication openings (access slits) between the substrate surfaces and processing chamber P can then be much smaller than the dark space distance of the plasma discharge maintained in the chamber. The surface processing used according to the invention is performed by the gas containing nitrogen that is excited by the discharge and enters the magazine through the abovementioned openings and slits.

It is readily apparent that the processing method used according to the invention is suitable for cleaning surface areas that are difficult of access on workpieces and/or substrates, for example edges, holes, blind holes, grooves, etc., said surface areas subsequently serving for an intimate

connection. Such surface areas are shown schematically in Figure 7.

A pumping system 42 is provided to pump down chamber 11 and possibly cathode chamber 1 as shown, with a pumping system 42a possibly being provided as well in order to pump down the cathode chamber separately. The diaphragm arrangement with diaphragm opening 9 act as the pressure stage between the pressure in the cathode chamber 1 and the pressure in the processing chamber 11.

The wall of cathode chamber 1 forms the ignition electrode: to ignite the low voltage discharge, the thermionic cathode 3 is heated to electron emission with heating current I_H and argon is admitted to the cathode chamber. Because of the distance ratio between the wall of cathode chamber 1 and cathode 3, as a result of the application of the potential of the latter, the discharge is ignited, whereupon a current i flows through unit 28, especially resistance 30. This reduces the potential Φ_z, previously at the ignition value, of the cathode chamber wall 17, with the wall of chamber 1 acting as an anode during operation only to a negligible degree and the primary discharge being drawn by the diaphragm arrangement with opening 9 to the anode 38 on the processing chamber side.

With a chamber like that shown in Figure 1,the surfaces of connecting workpieces were treated. These were for example:

— metal lead frames for soft soldering, for example made of copper, nickel plated-copper, and silver-plated copper,

— organic HLST materials, such as BGA ("ball grid arrays") and MCM ("multichip modules"), for example on an epoxy or ester basis, as well as

PCBs, "printed circuit boards");

— metallic QFP ("quad flat packs"), for example made of copper, silver-plated copper, or palladium-plated copper,

-- the metallization of the traces for the organic HLST materials and the QFP, for example made of silver-plated copper, gold-plated copper, or gold

— semiconductor substrate carriers designed as flip chip with soldering points made for example of AgSn, PbSn, PbSnAg, and PbInAg;

— HLST materials on a ceramic basis, for example aluminum oxide;

-- surface protecting layer of the chips, for example made of silicon nitride, silicon oxynitride, and polyimide;

-- directly bonded Si-Si wafers.

<u>Description of processing:</u>

The processing chamber according to Figure 1 which was used for the tests to be described had a volume of

$$V = 150 \text{ liters}$$

The workpieces of the type described above were placed in the chamber and the operation was as follows:

1. Pumping down to a basic pressure of approximately 10* mbar;

2. Activation of cathode 3 with I_H approximately 190 A;

2.1 Argon/hydrogen plasma (reference test)

Discharge current: Test I: 50 A

Test II: 60 A

Argon flow: 20 sccm

Processing time: Test I: 10 minutes

Test II: 10 and 20 minutes

2.2 Pretreatment in argon plasma (2d reference example)

Discharge current: Test I: 50 A

Test II: 60 A

Argon flow: 20 sccm;

Processing time: Test I: 10 minutes

Test II: 10 and 20 minutes.

2.3.2 Treatment according to the invention (combination of nitrogen and hydrogen).

Discharge current: Test I: 50 A

Test II: 60 A

Argon flow: 20 sccm

Nitrogen and hydrogen flows: total 20 sccm, 4 vol.% hydrogen .

Processing time: Test I: 10 minutes

Test II: 10 to 20 minutes

2.4. Pretreatment according to the invention (N_2 only).

Arc current: Test I:50 A

Test II: 60 A

Argon flow: 20 sccm

Nitrogen flow (pure): 20 sccm

Processing time: Test I: 10 minutes

Test II: 10 to 20 minutes.

In all cases, following a heating time of the thermionic cathode that was about 30 seconds, with a heating current of approximately 190 A, an ignition voltage between cathode 3 and ignition electrode 17 (see Figure 1) was applied. Resistance 30 was set to approximately 28 ohms and connected to ground. Following ignition of the discharge (ignition voltage approximately 20-30 V) a discharge voltage develops between cathode 3 and anode 38 of approximately 25 V at 50 A discharge current, with preferred use of a welding generator if the recipient wall 11, at ground, is used as the anode.

Ions and excited neutrons are generated for which the typical plasma glow is an indication. The workpieces to be processed in the magazines were surface-treated in the plasma thus produced. The nitrogen and possibly the hydrogen-volatile compounds with impurities were pumped off by pumping system 42.

The working pressure was approximately 5×10^{-3} mbar.

As shown in Figure 1, magazines 51 were used that had access slit widths H. (see Figure 1) from 1 mm to 10 mm.

Instead of the magazine and hence the workpieces being placed at ground

potential, the latter in particular (set to floating potential or to a different reference potential) are exposed to the plasma processing. The fact that the potential of the workpieces relative to the plasma potential in the low-voltage discharge described above is very low, 20 V or less, both the problem of redeposition of material on the workpieces as occurs in so-called free sputtering, and also in particular the danger of the destruction of integrated circuits that are critical with respect to electrical potential differences can be ruled out. Cleaning and preservation take place solely by chemical processes which are effected either by electrons, with workpieces suitably connected to potential, or by low-energy ions and electrons in workpieces that are operated to be floating.

The large number of electrons injected into the plasma ensures a high reactivity of the plasma, and hence short processing times, which is critical for the economy of the proposed method. Another advantage is that the plasma penetrates small hollow spaces especially in the magazine shown. Thus for example Workpieces can be processed without removing them from the cassette or magazine shown here, which is especially economical.

PBGA-HLST as well as "lead frames" with copper surfaces were processed as workpieces for subsequently producing a soft-soldered connection.

Results:

Figure 4 presents the tensile strength results. The tensile strength and pulling force F_P of the intimate connections were measured on the PBGA-HLST processed according to the invention, said connections being produced by gold wire bonding. Figure 3 shows this procedure schematically. 53 indicates the connecting point with the surface of a "lead

frame" 57a treated according to the invention.

The surfaces of the treated substrates had previously been treated by the manufacturers in unknown ways. Following this pretreatment, the danger of a redeposition from the gas phase, in other words plasma polymerization, on the surface was foreseeable.

On the substrates not subjected to further treatment, obtained directly from the manufacturers, no "wire bonding" connections were made. The resultant tensile strengths are shown in Figure 4 for Test I. The treated substrates are precisely the substrates that are unsuited for an argon/hydrogen plasma treatment: the feared redeposition from the gas phase, in other words plasma polymerization, did in fact occur during argon/hydrogen plasma treatment, as indicated by the relatively poor tensile strength results (a).

A tensile strength of approximately 3.3 cN was measured.

With treatment in argon plasma, a slightly better results (b) were obtained, with a tensile strength of approximately 3.6 cN. Evidently the simple heating of the substrate surfaces and the associated desorption alone produced better values than could be achieved in argon/hydrogen plasma because of plasma polymerization.

Definitely better results were measured as the result of treatment according to the invention, namely in an argon/nitrogen plasma with a low hydrogen component, in the present case approximately 4 percent according to (c) and in argon/nitrogen plasma according to (d). It should be noted at this point that if hydrogen is mixed with the gas G to be excited, which in any

event would result in a smaller amount that if the gas contained nitrogen.

In the substrates treated according to the invention, tensile strengths of approximately 5 cN (c) or far more than 5 cN were measured (d).

Basically, specified tensile strengths of 5 cN were usually required for the connections described.

Figure 5 shows the long-term effects of the cleaning effect for substrates which, as just described, were treated according to Test 1 (c), in other words in to argon/nitrogen/hydrogen (4 vol.%) plasmas.

On the one hand, the tensile strength F_P is reduced and on the other hand the storage time of the treated substrates in air up to the preparation of the "wire bondings.".,

It turns out that the measured tensile strength values remain unchanged within measurement accuracy for seven days, in other words there was no re-contamination of the surfaces exposed in the plasma processing procedure.

Figure 6 shows the results of Test II by analogy with the tests according to Figure 4. The results marked "*" were obtained with a 10-minute treatment, while those marked "**" were obtained with a 20-minute treatment. The discharge current as mentioned above was 60 A. The tests (a to d) according to Figure 6 and those according to Figure 4 correspond. In Figure 6 the tests on the substrates treated in Ar plasma are not shown but they were much worse than the tests according to (a), in other words in the argon/hydrogen plasma.

From this it is clear that despite a higher discharge current as compared with Test I, with a 10-minute processing in argon/hydrogen plasma (a), the required 5 cN tensile strengths were still not reached. For the plasma processing according to (c) and (d) however they have, even with the abovementioned 10-minute treatment at 60 A arc current, far above the required value, namely approximately 6.5 cN (c) and 6 cN (d). Thus, similarly good results can be obtained in argon/hydrogen plasma only by lengthening the processing time. This involves a higher thermal load on the substrates, and with a longer processing time undesired effects can occur on substrates with different additional material surfaces. While in substrates treated according to (c) and (d) according to the invention, no problems occurred with subsequent "molding," in the substrates (Figure 6) processed according to (a) a partial delamination of the "molding " material was observed. Precisely this indicates that even with respect to materials that are used, the processing method employed according to the invention has a wider processing window.

It is also important to note that the tensile capacity tests presented in Figure 6 were performed on substrates five days after their plasma processing according to the invention, while Tests I according to Figure 1 result during bonding on the same day on which the plasma processing was performed.

In Figure 2, finally, the Auger spectrum of copper surfaces ("lead frames") for producing a soft-soldered connection are shown.

Spectrum (8) was recorded on a "lead frame" not treated according to the invention.

Spectrum (b) was recorded following a 2-minute pretreatment according to

the invention according to Figure 4, Test I (d), spectrum (c) was recorded following a 4 -minute pretreatment of this kind, while spectrum (d) was recorded following a 6-minute pretreatment of this kind. It is particularly the development of the C peak at 271 eV and the N peak at 379 eV and the O peak at 503 eV that demonstrate the cleaning action of the method according to the invention. The substrates on which the spectra according to Figure 2 were recorded were treated for the described processing times in argon/hydrogen/hydrogen (4 %) plasma. With treatment in argon/nitrogen plasma according to (d) in Figures 4 to 6 the behavior relative to C and N remains essentially the same but oxygen is not completely reduced.

According to the invention, workpieces that have been treated in a plasma with nitrogen and then simply stored in air, as mentioned above, are marked by their significant surface nitrogen concentration.